NOTE

Indian J. Phys. **64B** (1), 63-65 (1990)

Theoretical evaluation of relaxation times of some aliphatic esters in different non-polar solvents at 40°C

Madhulika Khatry*, Gopal Lal Sharma and J M Gandhi
Microwave-Research Laboratory, Department of Physics,
University of Rajasthan, Jaipur-302 004, India

Received 17 January 1989, accepted 24 July 1989

Theoretical evaluation of relaxation times by five different methods namely Debye's τ_1 (Debye 1929), modified Debye's τ_2 (Fischer 1939), Sperhol and Wirtz's τ_3 (Sperhol and Wirtz 1953, Gieres and Wirtz 1953), Murty's τ_4 (Murty 1959) and Syamalamba and Premaswarup's τ_5 (Syamalamba and Premaswarup 1966) equations have been employed to make theoretical predictions and to compare these with the experimental results for the four systems containing allyl-methacrylate, *n*-butyl acrylate, isobutyl acrylate and isobutyl-methacrylate for which experimental values were available (Khatry and Gandhi 1987) at 9.92 GHZ in six different non-polar solvents at 40 °C.

The relaxation times calculated from five different equations are given in Table 1 alongwith the experimental values reported by Khatry and Gandhi (1987). The data recorded in the given Table 1 shows that for all the four esters in all the six solvents, the predictions of τ_1, by the Debye's equation (Debye 1929) are many folds of the actual experimental relaxation time values. The Debye's equation therefore, cannot be employed for the present systems. This is as expected since the four esters under study do not have spherical molecular shape, while the Debye's equation is applicable to the spherical molecules only.

The same table shows that the theoretically predicted values τ_2 are also many times higher than the experimental ones. The modified Debye's equation (Fischer 1939) is therefore, certainly an improvement over the Debye's equation (Debye 1929) but it still remains totally inadequate to represent the relaxation behaviour of compounds under the present investigations. This is again as expected because in this equation, although the viscosity of the medium has been modified to have a better representation of the resistance of the internal viscosity to the rotation of the polar molecules, but no account of the deviation from the spherical shape of the molecules has been taken.

*Present Address : Government College, Barmer, Rajasthan, India.

The Table 1 shows that the equations of Sperhol and Wirtz (1953), Gieres and Wirtz (1953) and Syamalamba and Premaswarup (1966), can predict the relaxation time values far better than the Debye's and the modified Debye's equations. Although the theoretically calculated values of τ_3 and τ_5 are nearer

Table 1. Experimental relaxation time τ_0, and theoretical relaxation time τ_1, τ_2, τ_3, τ_4 and τ_5 values in ps for the four aliphatic esters in different non-polar solvents at 40°C.

Solvent	τ_0	τ_1	τ_2	τ_3	τ_4	τ_5
		Solute : Allyl-methacrylate				
n-Heptane	3.9	55 3	19.9	6 7	5.5	7.2
Benzene	5 6	80.0	28 8	11 3	7.2	12 1
Cyclohexane	7 2	111 7	40 2	14 9	10.7	15.4
Carbon-tetrachloride	10 0	124.6	44 9	17 2	11.4	18 5
1,4-Dioxane	10.3	147.9	53.2	21.2	13.5	21.9
Decalin	11.5	293.0	105.5	34.8	27.1	42.8
		Solute . Butyl-acrylate				
n-Heptane	2.4	56 6	20.4	6 9	5 4	7 4
Benzene	5 2	82 0	29.5	11 7	7.2	12.4
Cyclohexane	6.3	114.5	41.2	15.4	10.6	15.8
Carbon-tetrachloride	8 7	127.7	46 0	17.8	11 3	19 0
1,4-Dioxane	10.8	151.6	54 6	22 0	13.4	22 5
Decalin	8 7	300.4	108 1	36.0	26 9	43.9
		Solute : Isobutyl-acrylate				
n-Heptane	4 0	57.3	20.6	7 0	5 4	7 5
Benzene	5 6	83 0	29.9	11.8	7 2	12.5
Cyclohexane	7.1	115.8	41 7	15 6	10 6	16 0
Carbon-tetrachloride	11 4	129.2	46 5	18.0	11 3	19 2
1,4 Dioxane	10 4	153 4	55.2	22.2	13 4	22 7
Decalin	9.0	303.8	109 3	36.4	26 9	44 4
		Solute . Isobutyl-methacrylate				
n-Heptane	6 9	63 6	22 9	8 1	6.1	8.3
Benzene	9.4	92 2	33.2	13 6	8 1	13.9
Cyclohexane	9.3	128.6	46 3	17.9	12.0	17.8
Carbon-tetrachloride	12.3	143.5	51.7	20.7	12.7	21.3
1,4-Dioxane	13.5	170.3	61.3	25.6	15.1	25.2
Decalin	8.4	337.5	121 4	42 0	30.3	49 3

to the experimentally determined values. The discrepancies are still large and can be supposed to be due to (i) the large deviations of the molecular shape from the spherical shape and (ii) the existence of internal rotations which have not been considered in the development of both of these equations.

The Table 1 also shows that the Murty's equation employed for calculating the relaxation time τ_4 value predicts the relaxation behaviour slightly better than the other two equations for the systems under present investigations. It may further be pointed out that predictions by all the three equations are more close to the experimental results for the solvents of low viscosity only. The small deviations of the theoretical values from the experimental ones in the less viscous media may be attributed to the fact that the presence of specific solute-solvent interactions and internal rotations in the molecules concerned have not been taken into account in these equations. In the more viscous solvents the τ_4 value are also 2.7 to 3.9 times of the τ_0 values, again suggesting that in more viscous solvents, macroscopic viscosity of the solvent should rather be replaced by a frequency dependent dynamical viscosity. This may therefore, be concluded that all the three viz. the equations of Sperhol and Wirtz (1953), Gieres and Wirtz (1953), Murty (1959) and Syamalamba and Premaswarup (1966) provide a rough representation of the relaxation behaviour in the less viscous media only, but none of these equations are capable of correctly predicting the relaxation behaviour of the molecules under present study in the more viscous solvents. Further, the Murty's equation is a slightly better representation of the relaxation phenomena of the polar substances in the non-polar solvents.

Acknowledgments

The authors are thankful to the Head of the Department of Physics, University of Rajasthan, Jaipur for providing the Laboratory facilities. One of us (G L S) is thankful to the CSIR, New Delhi, for awarding the Senior Research Fellowship.

References

Debye P 1929 *Polar Molecules* (New York : Chemical Catalog) *Chap.* 5
Fischer E 1939 *Phys. Z.* **40** 645
Gieres A and Wirtz K Z 1953 *Naturf.* **8A** 532
Khatry M and Gandhi J M 1987 *Indian J. Phys.* **61B** 96
Murty C R K 1959 *Indian J. Phys.* **32** 580
Sperhol A and Wirtz K Z 1953 *Naturf.* **8A** 522
Syamalamba K and Premaswarup D 1966 *Indian J. Pure Appl. Phys.* **4** 84